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REVIEW ARTICLE

Adsorptive Remediation of Heavy Atoms Contaminated Water Using Graphene Oxide: A Review

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Abstract: The use of graphene-related two-dimensional (2D) materials in water treatment have gained tremendous attention in diminishing the worldwide water scarcity owing to their unique water transport properties, high surface area, excellent mechanical strength, non-corrosive features and tunable surface chemistry as discussed in patents. Graphene oxide (GO) has also received extensive coverage in water treatment processes as a promising adsorbent candidate because of its higher adsorption capacity for the removal of several hazardous contaminants. Compared to the conventional adsorbents, GO may offer several advantages; such as two basal planes available for toxin adsorption, scalable production, oxygen-containing functional groups and catalyst free conditions. The current review is focused on the synthesis methods, chemical, and adsorption properties of GO, and their applications for the removal of heavy metal species.

Keywords: Graphene, heavy atoms, graphene oxide, adsorption, two-dimensional, remediation.

1. INTRODUCTION

The 21st century has been called the Century of the Environment [1]. Rapid increase in world population, technological and industrial revolution, the impurity of aquatic systems and ecological concerns are all becoming a main motivation of the scientific consideration to alleviate health and ecological related implications [2]. The magnification of wastewater release to the environment and circulation of hazardous materials in water have been boosted in recent years [3, 4], and as a result, it has long term complications and significant effects on human physiology. Heavy metal species are not easily biodegradable and their accumulation in living organisms has profound biotechnological implications [5]. The toxicity and potential consequences of these heavy metal species pose a severe danger to both groundwater and surface water and the removal of such pollutants including heavy metal ions from water have become a critical issue. Adsorption is commonly used method for the removal of such harmful materials and is the most widely used technique as an efficient, low-energy and cost-effective treatment process which provides a better selectivity for multivalent ions when compared with conventional methods used for the elimination of heavy metal ions in water and wastewater [6]. The most important features of a good adsorbent are: high specific surface area, high porosity with specific adsorption vacancies, pH-dependent surface charge, cost-effective production routes, facile regeneration and reusable capacities and high ion exchange capability [7]. Conventionally used adsorbents include clay mineral [8], activated carbon [9], zeolites [10] and metal oxides [11], and apart from these adsorbents, nanomaterials (NMs) such as carbon nanotubes (CNTs), graphene and its 2D counterparts have also gained much attention recently for the remediation of environmental problems [12]. Although the adsorption capabilities of nanomaterials (NMs) rely on their structural morphology and surface characteristics [13], NMs appear to be a better choice in exploiting their unique features for removal of such toxins from water. NMs have several applications in water filtration, separation and treatment. In general, the effectiveness of NMs for water treatment is mainly related to their surface area, adsorption capacity, structural morphology, and their synthesis mechanism, and chemical and mechanical behaviour. In this regard, a variety of adsorbents have been investigated to remove toxic heavy metal ions in water in the last few decades, such as activated carbon [14], magnetic carbon [15], sand [16], chitosan [17] and clay [15]. Compared with conventional materials, nanoadsorbents exhibit much higher adsorption capacities and faster reusability in water and wasterwater cleaning as they possess a wide range of physicochemical characteristics. It is evident that carbon-based materials and graphene-related materials can be synthesized in large scale in an environmentally friendly method to reduce their preparation cost and thereby enhance their use to protect the environment [18].

Graphene, a 2D monolayer sp^2 hybridized carbon atom with honeycomb structure, is a promising candidate for multiple applications [19] owing to its specific surface area [20], high Young's modulus, thermal conductivity [21], high intrinsic mobility [20], and optical and mechanical properties

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[22]. Graphene oxide (GO) is a graphene-based composite with oxygen-containing functional groups on their surface. Recently, graphene-based nanocomposites have also been exploited for the removal of these toxic contaminants from aqueous solutions. Among 2D materials, GO is an ideal candidate for water cleaning which is attributed to its superior physicochemical features induced by oxygen-containing functional groups such as hydroxy, epoxy on the basal plane and carbonyl, carboxylic acid at the edges [23]. Through the sharing of the free electron pair on oxygen, it can proficiently bind the metal ion to form a metal complex, thereby, adapting it as an effective adsorbent for the elimination of heavy metal ions. These functional groups have great potential for generating strong bonds with water molecules which in turn provide a good dispersion and stability in water solutions. Furthermore, these groups have a negative surface charge, resulting in a good selectivity of positively charged ions from aqueous solutions. Based on the high surface area, scalable production, tunable surface chemistry, non-corrosive nature, high Young's modulus, remarkable electronic, optical, and thermal properties, chemical and mechanical stability and the presence of functional groups of GO, its adsorption capacity has recently been reported better than other conventional adsorbents, such as zero valent iron, iron oxide, zeolite, silica, titanium dioxide, chitosan, and polymer [24]. Based on the potential advantages of GO, we present a brief overview of the latest progress made in GO nanocomposites for the adsorptive remediation of heavy metals in water, mainly focusing on their mechanisms and advantages for adsorption of heavy metals. In the last section, we propose some interesting research prospects in the field of water treatment using nanostructured adsorbents.

2. SYNTHESIS AND STRUCTURE OF GO

The most commonly used GO synthesis methods are chemical oxidization of graphite flakes including Hummer's method, modified Hummer's method and the Tour's method [25], (see Fig. **1** for a comparison of these methods). Hummer's method involves the addition of $KMnO_4$ to graphite flakes, H_2SO_4 and HNO_3 are added in an ice bath and the mixture is magnetically stirred. The as-prepared material is stirred for two additional hours until it turns brown followed by the addition of H_2O_2 which not only removes the residuals but also enables the transition in colour to brown. On the other hand, the modified Hummers' method has some variations in mixture ratio of $KMnO_4$ and graphite flakes [25] and occasionally $K_2Cr_2O_7$ is also used instead of $KMnO_4$ as described in [26]. Fig. (**1**) shows a schematic representation of the different routes of synthesis and Fig. (**2**) illustrates the structure of graphene, GO and reduced graphene oxide (RGO) and scanning electron microscope (SEM), x-ray diffraction (XRD) patterns, and the dynamic rheological behaviour of GO. SEM images of GO network have been shown in Fig. (**2d** and **e**), and the ssDNA bridging as the driving force for self-assembly of GO and DNA (further confirmed by the X-ray diffraction (XRD) patterns) has been shown in Fig. (**2f**) in which the strong characteristic 2 peak for GO appears at 10.6°, corresponding to a layer-to-layer stacking distance of 8.34 Å.

3. REMOVAL OF HEAVY METAL IONS BY GO ADSORPTION

Heavy metals in wastewater include As, Cu, Pb, Cd, Zn, Cr, Co, Ni and Ag and for the removal of these species, carbon-based materials such as activated carbon [14], CNTs [27] and graphite [28, 29] have been extensively explored in recent years. GO also offers strong adsorption capacity for the removal of these ions when compared with other carbon-based materials such as activated carbon and CNTs. As an adsorbent, GO removes selective metal ions through both ion exchange and electrostatic approaches (see Table **1** for the adsorption capacities of GO, RGO, and several metals oxides on GO, for remediation of metal species from aqueous solutions). Yang *et al*. [30] used GO for the removal of Cu ions in aqueous systems with an adsorption capacity of 46.6 mg/g. Cu (II) stimulates GO sheets to form large aggregates, and this aggregation is most likely caused by the distribution and stacking between GO sheets and Cu (II). In addition, oxygen-containin functional groups on GO surface also play an important role in the removal of contaminants. The adsorption capacity of GO-based adsorbents and the mechanism involved in the removal of Pb and Hg have been

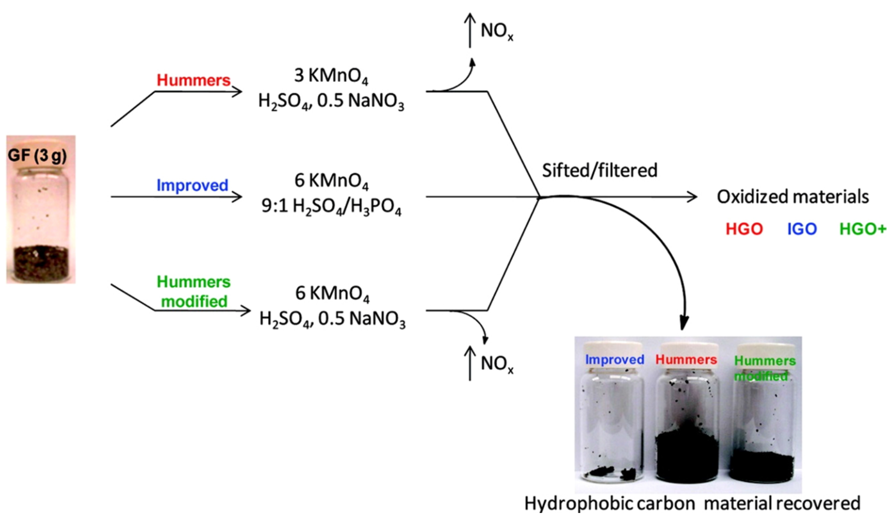

Fig. (1). Representation of the synthesis of GO starting with graphite flakes as raw materials for Hummers, Improved Hummer (known as Tour's method) and modified Hummer's methods [25]. Copyright 2010, American Chemical Society.

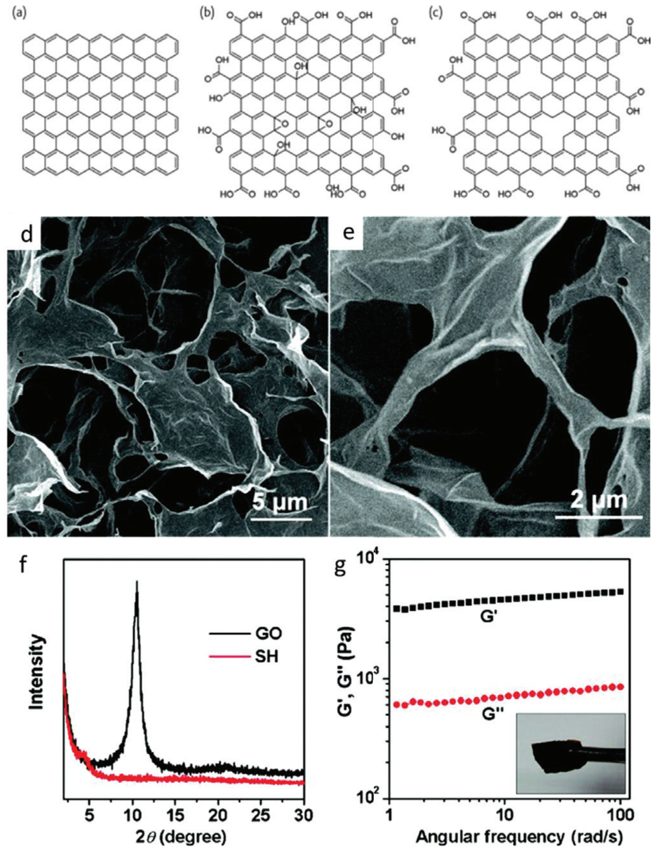

Fig. (2). Structural models of (**a**) graphene, (**b**) graphene oxide (GO) (**c**) reduced graphene oxide. Reproduced with permission [27] Copyright 2014, John Wiley and Sons. SEM images with low (**d**) and high (**e**) magnifications of GO/DNA interior microstructures; (**f**) XRD patterns of freeze-dried GO and GO/DNA SH; (**g**) dynamic rheological behaviour of the typical SH prepared from the mixture of GO and dsDNA. The inset shows a free-standing GO/DNA SH. Reproduced with permission [28] Copyright 2013 Elsevier.

summarized in Table **1**. The existence of oxygen-containing functional groups reveals a distinctive capacity for the functionalization and modification of GO. For example, by attachment of other NMs to GO, stacking of GO sheets can be avoided and therefore, the functionalities can give good adsorption properties of individual GO sheets.

The mechanism of the functionality of GO and its applications as a heavy metal removal agent has also been the subject of various studies. The functionalization and chemical modification of GO with different metal oxides such as TiO_2 and Fe_2O_3 can alter their surface chemistry to improve the adsorption efficiency of metal ions. In 2011, Lee *et al.* [29] prepared TiO_2/GO for the removal of Zn (II) and Pb (II), and it was shown that TiO_2 on GO significantly improved the removal efficacy. In the same year, Liu *et al.* [31] fabricated magnetite/GO composite for the removal of Co (II) in water. Chitosan is a broadly utilized adsorbent for the removal of metal species, and the chemical functionalization of chitosan with GO can enhance the removal efficiency and adsorption strength. The fabrication of microporous chitosan/GO composite for the adsorption of species such as Pb (II) was further shown by He *et al.* in [32].

4. ADSORPTION MECHANISM

As a relatively new adsorbent, GO has significantly been exploited for the removal of heavy metal ions in water treatment due to the unique structural, electronic, thermal, mechanical, chemical and physical characteristics [33]. GO can be divided into two main groups, *i.e.* pristine GO and functionalized GO. The selectivity and adsorption of heavy metal ions by GO usually takes place through electrostatic attraction and surface ion exchange between functional groups (existing on the surface of GO) and pollutants, and the mechanism of adsorption is generally determined by the pH, surface charge, surface groups and metal specification [34]. In the case of GO as an adsorbent, electrostatic attraction is more evident because of the epoxy, carboxyl, and hydroxyl groups on the surface of GO which plays a vital role in the removal and adsorption of metal ions. For example, Zhang *et al.* [35] synthesized reduced GO grafted by 4-sulfophenylazo groups for the adsorption of ions (Pb(II), Cu(II), Ni(II), Cd(II) and Cr(III)) in an aqueous solution *via* two kinds of adsorption modes, i.e. ion exchange and coordination, and it was shown that the maximum adsorption capacities for Pb(II), Cu(II), Ni(II), Cd(II) and Cr(III) were 689, 59, 66, 267 and 191 mg/g, respectively. Table **1** presents a more detailed review of GO for the removal of heavy metal ions in water [29-38].

CONCLUSION AND FUTURE PERSPECTIVES

Safe drinking water has a significant effect on all aspects of human life, such as health, food, energy, economy and the environment. A regular and surplus supply of safe water has become a global challenge due to climate change, urbanization and increasing populations. Nanotechnology is playing a vital role in water treatment owing to the unique properties of NMs, such as high specific surface area, nanoscale features, and electronic, chemical and mechanical characteristics. These characteristics make NMs ideal candidates for water treatment options including adsorption, membrane technology and biological/tertiary treatment. This mini review has provided key insights into the use of GO for the removal of heavy metal toxic ions for drinking water treatment.

GO are newly synthesized fascinating materials having a relatively high surface area and oxygen-containing functional groups. The use of GO can enable the reduction of a variety of organic and inorganic pollutants and toxins in real-world applications. GO certainly has excellent properties for water treatment but much more efforts are required to develop highly efficient methods to further improve their surface area, adsorption capacity, and recyclability/regeneration efficiency. Surface modification of various types of graphene and their nanoderivatives can potentially result in improved water quality and control to enhance the selectivity and reactivity of toxins found in drinking water particularly in developing countries. Despite high adsorption capacities and other aforementioned suitable properties, GO has some disadvantages: (i) possibility of leaching of GO nanostructures owing to its high affinity towards water and (ii) high cost of synthesis [39]. Surface modification and functionalization of GO can be carried out by incorporating a variety of other nanoparticles such as TiO_2 and single and multiwalled

Table 1. Graphene-based nanocomposites for removal of heavy metal ions with their respective adsorption capacities and the mechanisms involved in these processes.

GO-based Adsorbent	Mechanism Involved in the Adsorption of Metal Ions	Metal	Adsorption (mg/g)	Refs.
GO	Electrostatic interactions	Cu (II)	46.6 (RT)	[29]
GO	Electrostatic interactions	Cd (II)	106.3	[36]
GO	Electrostatic interactions	Co (II)	68.2	[36]
GO	Ion exchange	Pb (II)	35.6 (RT)	[37]
GO	Ion exchange	Hg (II)	35 (RT)	[30]
TiO_2 GO	Ion exchange	Zn (II)	88.9	[31]
TiO_2 GO	Ion exchange	Pb (II)	65.6	[37]
Fe_3O_4/GO	Electrostatic interactions	Co (II)	22.7	[31]
GO/chitosan	Electrostatic interactions	Pb (II)	99 (RT)	[32]
GO-gelatin/chitosan	Electrostatic interactions	Cu (II)	120 (RT)	[38]

CNTs which may lead to the improved surface area and a subsequently enhanced uptake of emerging contaminants. Surface functionalization can also enhance the generation of free radicals and reactive oxygen species, as well as an increase in reactivity towards a wide range of pollutants. GO can also be functionalized to improve its properties, such as the selectivity of ions, loading ability, solubility and biocompatibility. Functionalized GO presents advantages such as (i) no leaching of GO nanostructures; (ii) facile regeneration and (iii) cost-effective synthesis [40].

Recently, magnetic adsorbents have also been explored for water treatment. The incorporation of magnetic particles in GO structures provides an efficient approach to overcome the problems associated with separation of GO from aqueous solutions [41]. Additionally, magnetic NMs can also reduce the possibility of agglomeration and aggregation of GO layers to achieve maximum adsorption capacity. However, adsorption kinetic models such as pseudo-first-order, pseudo-second-order Langmuir, intraparticle models etc need to be employed to better understand the mechanism and role of the structural morphology of nanostructures in the adsorption of contaminants. In addition, further investigations are also required to use graphene in filtration and membrane technology for the successful application of novel graphene nanostructures for real-world applications. Moreover, mesoporous three-dimensional graphene foam has a higher surface area and excellent mechanical strength when compared with GO but these materials have largely been underexplored so far. We have recently reported the biocompatibility and toxic effects of three-dimensional graphene foam and RGO which showed that three-dimensional porous graphene frameworks and RGO are biocompatible for use in environmental applications [42, 43]. Globally, vast numbers of patents, each one demonstrative of intellectual property, have already been filed mainly focussing on graphene-based materials for environmental clean-up [44, 45]. For example, one patent explains the reduction of GO membrane to form RGO membrane for water cleaning and water/oil emulsion *via* passing through RGO membrane [46].

The biocompatibility of adsorbents is also an important feature and must be taken into account as such adsorbents release ions in water making them unsafe to drink. Further studies are also required to explore the availability of graphene in environment. There is a knowledge gap in exploring the availability of adsorbent materials before using them in water remediation. These porous graphene nanostructures can help degrade a variety of organic contaminants in industrial wastewater. For realistic applications, one of the greatest challenges lies in how to accomplish their cost-effective performance in water treatment. Activation of GO and RGO into a porous architecture may also be a promising approach to further improve the adsorption capacity.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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